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FINAL YEAR PROJECT 2: DISSERTATION

DEVELOPMENT OF REACTION KINETICS MODEL FOR THE PRODUCTION OF SYNTHESIS GAS FROM CARBON DIOXIDE CO_2 (DRY METHANE REFORMING)

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(Chemical Engineering)
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CERTIFICATION

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

Increasing problems related with climate change and global warming has lead Carbon Dioxide (CO_2) reducing technologies that have receive many attentions. Carbon Dioxide (CO_2) has been identified as the most major greenhouse gas (GHG_S) arising from anthropogenic activities. It is very important to reduce anthropogenic Carbon Dioxide (CO_2) emissions in order to counteract global warming. This reaction has very important environmental implications since both Methane(CH_4) and Carbon Dioxide (CO_2) that dominantly produced from municipal solid waste (MSW) contribute to the greenhouse effect. Converting these gases into a valuable feedstock may significantly reduce the atmospheric emissions of Methane(CH_4) and Carbon Dioxide(CO_2). Due to this condition as develop by past researcher, the efficient commercial production of syngas or synthesis gas (a mixture of Hydrogen H_2 and Carbon Monoxide CO) is gaining significant attention and consideration worldwide as it is a versatile feedstock that can be used to produce a variety of fuels and chemicals such as Methanol, Fischer-Tropsch fuels, Hydrogen H_2, Ethanol and Dimethyl Ether (DME). This mixture of Hydrogen H_2 and Carbon Monoxide CO can be produced by natural gas reaction which is Dry Methane reforming between Carbon Dioxide (CO_2) and Methane(CH_4). The Dry Methane Reforming reaction mechanism is considered quantitatively with four reactions which are Carbon Dioxide (CO_2) reduction by Methane (CH_4), Reverse Water Shift Gas (RWSG), Carbon Deposition and Carbon removal by a reverse Boudourd reaction. Hence, in this paper we present a comprehensive review on the characteristics of Dry Methane Reforming mechanism that can be used as basic references for future case review. Modeling and simulation of the reforming behavior of mixture Carbon Dioxide (CO_2) and Methane(CH_4) was introduced. The Dry Methane Reforming (DMR) process was simulated using MATLAB simulation software. The stimulated data were evaluated and validated with the previous literature review. A detailed simulation studies is used to identify the essential characteristics of reaction mechanism of Dry Methane Reforming (DMR). The results showed that inlet gas flow in gas phase effect has significant effect to the reactions whereas inlet molar composition ratio of the reactions was found to have no significant effect on the mechanism of Dry Methane Reforming.

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ABBREVIATIONS & NOMENCLATURES

UTP	*Universiti Teknologi Petronas*
CO_2	*Carbon Dioxide*
CO	*Carbon Monoxide*
H_2	*Hydrogen*
CH_4	*Methane*
SYNGAS	*Synthesis Gas*
GHGs	*Greenhouse Gases*
DMR	*Dry Methane Reforming*
K	*Reaction Rate Constant*
Ea	*Activation Energy*

CHAPTER 1: INTRODUCTION

1.1 Background of Study

Crucially important building blocks of the chemical industry are Carbon Monoxide (CO) and Hydrogen (H_2) which are used in a variety of processes. The production of are Carbon Monoxide (CO) and Hydrogen (H_2), synthesis gas (Syngas), is carried out by the steam reforming of methane, partial oxidation of fuel oil, and coal gasification. Synthesis gas is usually used and can be converted into petrochemicals, higher alcohols and synthetic fuels. Hydrogen is used ammonia synthesis and petroleum refining industries, while carbon monoxide is widely used in the production plastics, paints, foams, pesticides and insecticides. Common names for mixtures of CO/H_2 are derived from their origin such as "water gas" ($CO+H_2O$) from steam gasification of coal and "crack gas" ($CO+3H_2$) from the steam reforming of Methane, or from their application such as "Methanol synthesis gas" ($CO+2H_2$) for the manufacture of Methanol and "oxo gas" ($CO+H_2$) for hydroformylation reactions. Another synthesis gas is ammonia synthesis gas (N_2+3H_2) which does not contain CO as higher constituent. Initially, the manufacture of synthesis gas was carried out by gasifying coke from coal at low temperature with air and steam. Coal gasification dates back to and continued throughout the 1800s when it was used for heating and lighting in both industry and private sectors. By 1920, there were over 11,000 coal gasifiers in the United States. However, the inefficient processes were replaced in the 1940 by oil and gas. Oil and natural gas became commonly employed as a synthesis gas feedstock due their ease of handling and high hydrogen content. In the 1990s,

Methane reforming is still the predominant method of producing syngas, supplying more than 80% of the world's synthesis gas (Anderson et al. 1984). It is currently the most cost effective method of synthesis gas production and gas production includes naphtha reforming, fuel oil partial oxidation and coal gasification. Dry reforming of methane (DRM) is a process that uses waste Carbon Dioxide (CO_2) to produce syngas from natural gas. Dry reforming of Methane (DMR) to synthesis gas is an interesting way to

utilize and decrease two important greenhouse gases which are Carbon Dioxide (CO_2) and Methane(CH_4). Catalytic reforming of Methane with Carbon Dioxide, also known as "dry reforming of Methane" which is really a promising process for simultaneous chemical transformation of two major greenhouse gases, Carbon Dioxide (CO_2) and Methane(CH_4) to syngas, which can be used in a variety of downstream processes such as Methanol production, Fischer-Tropsch synthesis processes and in carbonylation, hydrogenation and hydroformylation processes.

Currently, in industrial business it is crucial to minimize cost in terms of operation or utilities and maintenance cost while maintaining the efficiency of the column operation and mass production. Throughout this environment problems with uncontrolled release of two major greenhouse gases which are, Carbon Dioxide (CO_2) and Methane(CH_4) from many various sources can be reduce by introduced the new reaction which is Dry Methane Reforming which are more environmental friendly from others method. Simulation study of Dry Methane Reforming (DMR) has a good track in terms of design parametic study as it provides good inter-related parameters process for basic and future referneces. By using Dry Methane Reforming, the existence of problems commonly in the waste disposal center (Landfills) can be overcome by optimize the used of Carbon Dioxide (CO_2) and Methane(CH_4) production from solid waste at the disposal site.

What is a landfill? A landfill site also known as a tip, dump, rubbish dump or dumping ground. Site for the disposal of waste materials by burial and is the oldest form of waste treatment. Historically, landfills have been the most common method of organized waste disposal and remain so in many places around the world. Some landfills are also used for waste management purposes, such as the temporary storage, consolidation and transfer, or processing of waste material (sorting, treatment, or recycling). A landfill also may refer to ground that has been filled in with rocks instead of waste materials, so that it can be used for a specific purpose, such as for building houses. Unless they are stabilized, these areas may experience severe shaking or liquefaction of the ground during a large earthquake. From this project, gaseous produced from landfills is important for the conversion to some value added product.

Dry Methane Reforming (DMR) tends to minimize the cost, but the same time maximize and utilize the two major greenhouse gases which are, Carbon Dioxide (CO_2) and Methane(CH_4) to form more valuable product which is Hydrogen that meet the market demands.

1.2 Problem Statement

Landfill gas productions which are mainly consist of Carbon Dioxide (CO_2) and Methane(CH_4) is generated through the degradation of municipal solid waste (MSW) by microorganisms. Landfill gas is approximately 40% to 60% Methane(CH_4), with the remainder being mostly Carbon Dioxide(CO_2). Due to the frequent production of landfill gas, the increase in pressure within the landfill causes the gases release into the atmosphere that mainly affect the climate change and global warming. Such emissions lead to important environmental, hygiene and security problems in the landfill. Due to the risk presented by landfill gas there is a clear need to monitor gas produced by landfills. Dry reforming is nowadays becomes alternative method using of Carbon Dioxide (CO_2) and Methane(CH_4) utilization. Several reaction involve in this dry methane reforming was investigated. The kinetics study of this reaction is very important for better production of Carbon Monoxide (CO) and Hydrogen(H_2). Simulation study of Dry Methane Reforming (DMR) Kinetics model has a good track in terms of design parametic study as it provides simultaneous of specific equations and a very important reaction.

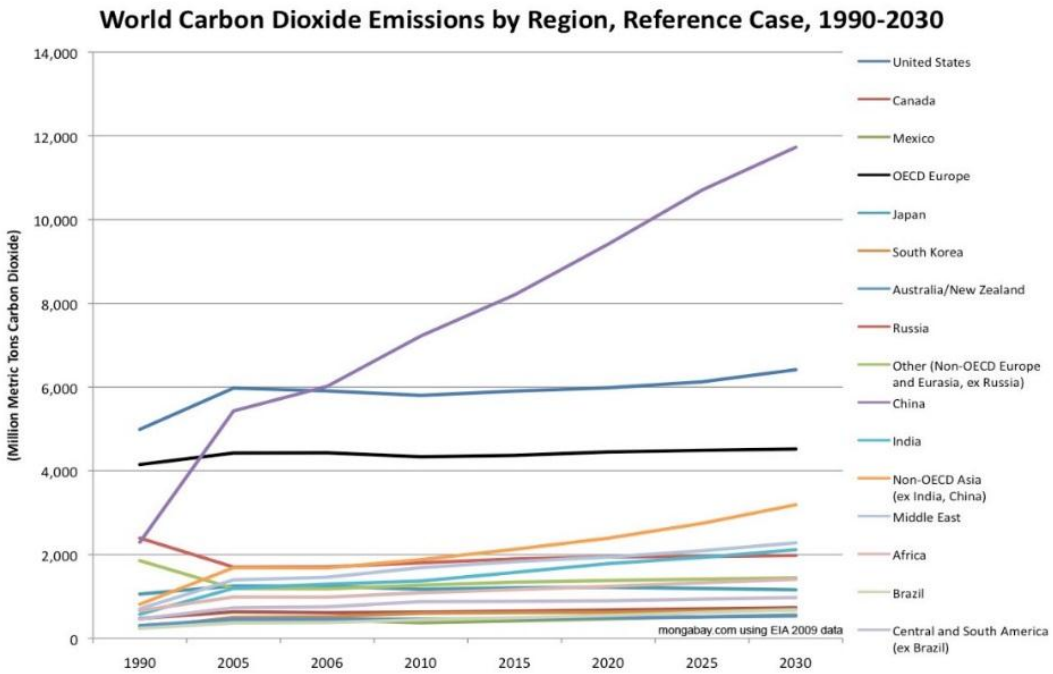


Figure 1: *Sources of world's Carbon Dioxide emissions*

1.3 Objectives

- To develop the reaction kinetics model for the Dry Reforming of Methane.
- To perform parametric study for the hydrogen production from Carbon Dioxide (CO_2) and Methane(CH_4) utilization.
- To calculate the reaction kinetics constant using optimization approach (MATLAB simulation).

1.4 Scope of Study

In the research, one particular process has to be chosen. The process will have its own model to indicate the process. The aim of this work was to simulate Dry Methane Reforming (DMR) processes and to conduct critical analysis and parametric study regarding the reaction rate constant(k). The study will involve in researching the potential way of producing Syngas, or synthesis gas. Other than that, the studies also investigate the effect of Dry Methane Reforming on various parameters that will be evaluated by the method of equilibrium constants which is the calculation on reaction rate constant(k). Syngas will be form by catalytic reforming of Methane with Carbon Dioxide in presence of metal based catalyst. The parametric of the whole Dry Methane reforming (DMR) production process will be analyses and the reaction rate constant(k)of each step of reaction will be calculated through Simulation MATLAB. The parameter will be varying to get the best and optimum production process. The parametric study will focus more on;

- Temperature
- Pressure
- Composition of feeds ($\mathbf{CH_4/CO_2}$) ratio and products ($\mathbf{H_2/CO}$) ratio of the reactions

CHAPTER 2: LITERATURE REVIEW & THEORY

2.1 Syngas (Synthesis Gas) definition

In this report, synthesis gas or syngas is defined as a gas that contains a mixture comprising of Carbon Monoxide(CO), Carbon Dioxide(CO_2), and hydrogen (H_2) main components. Raw syngas mostly inevitably contains also considerable amounts of Carbon Dioxide(CO_2), and hydrogen (H_2). The syngas is produced by gasification of a carbon containing fuel to a gaseous product that has some heating value. The name comes from its use as intermediates in creating synthetic natural gas (SNG) and for producing ammonia or methanol. Since the synthesis gas is produced from greenhouse gases that produced from landfills gas, this syngas is called Bio-syngas that is chemically identical to syngas, but is produced from biomass gasification through dry methane reforming.

2.2 Syngas (Synthesis Gas) Market

Nowadays, syngas is a significant intermediate product in chemical industry. Once a year, a total of about 6 EJ of syngas is produced worldwide, corresponding to almost 2% of the present total worldwide primary energy consumption. The world market for syngas (mainly from fossil energy sources like coal, natural gas and oil/residues) is dominated by the ammonia industry. Other main applications are the production of hydrogen for use in refineries, e.g. hydrogenation steps, and for the production of methanol. Figure 2.1 shows the present syngas market distribution.

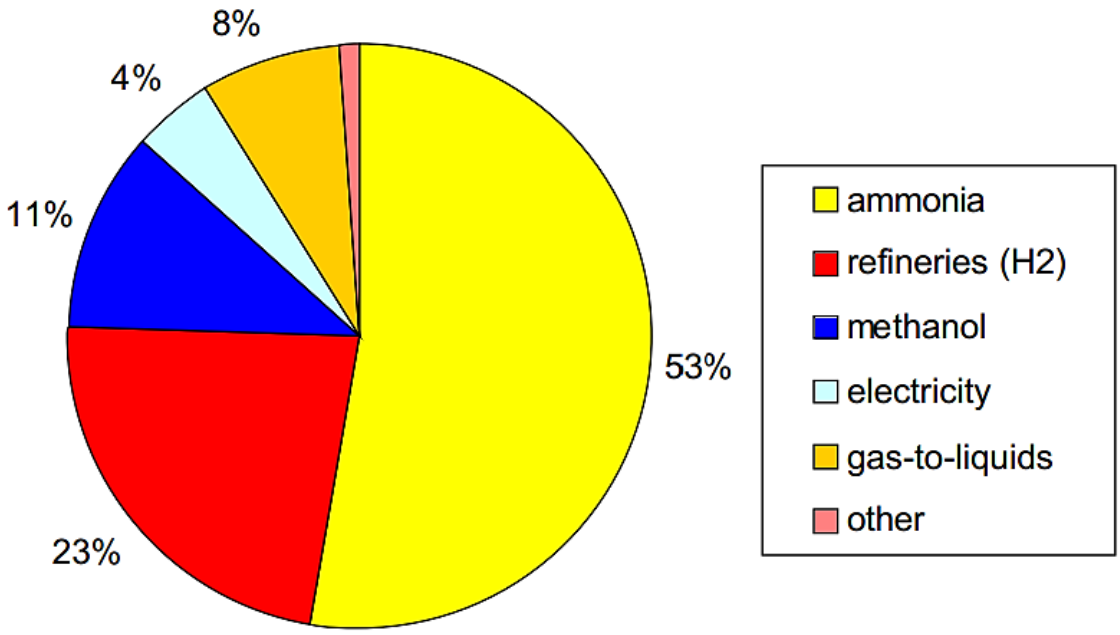


Figure 2: *Present world syngas market, totally ~6 EJ/y (Van Der Drift et. al 2004)*

Nowadays, global use of syngas for the production of transportation fuels in the so-called "gas-toliquids" processes (GtL) correspond to approximately 500 PJ per year. For example, it produced from the Fischer-Tropsch processes of Sasol in South Africa and of Shell in Bintulu, Malaysia. In the future, syngas will become gradually significant for the production of cleaner fuels to fulfill with the rigorous emission standards. Syngas is the intermediate energy carrier for the production of second generation biofuels like methanol, DME, cellulosic ethanol, and Fischer-Tropsch diesel. The huge potential market for syngas is shown by the fact that almost 20% of the present world primary energy consumption is for transportation fuels only (Van Der Drift et. al 2004). If the chemical sector is included, the total global syngas potential increases to approximately 30%. Biomass is heading for a great future as renewable energy source. It not only is available in large quantities, it also is the only renewable energy source that is suitable for the sustainable production of (generally carbon containing) transportation fuels and chemicals. Thus, the application of biomass as feedstock for the production of fuels and chemicals allows the reduction of fossil fuel consumption and the accompanying CO_2 emissions.

2.3 Biomass Gasification

Currently, there is a wide variety of biomass resources available to be converted into energy. (Khalid Al-Ali, 2014) classified this biomass into four general categories:

I. Energy crops: herbaceous energy crops, woody energy crops, industrial crops, agricultural crops and aquatic crops.
II. Agricultural residues and waste: crop waste and animal waste.
III. Forestry waste and residues: mill wood waste, logging residues, trees and shrub residues.
IV. Industrial and municipal wastes: municipal solid waste (MSW), sewage sludge and industry waste.

For this project, the feedstock gas such as carbon dioxide and methane are produced from landfills that are considered as an industrial and municipal solid waste (MSW). Gasification is a process that converts organic or fossil fuel based carbonaceous materials into carbon monoxide, hydrogen and carbon monoxide. This is achieved by reacting the material at high temperatures (more than 700 °C), without combustion, with a controlled amount of oxygen and/or steam. In this report, instead of using steam methane reforming as a main process of biomass gasification, the dry methane reforming is chosen as it is more economically friendly. Since, the process of steam reforming is rather expensive, the other three types of catalytic chemical processes are considered as alternative processes for carrying out the reforming of methane, and they were developed with the aim of making savings in thermal energy consumption required by these catalytic processes.

Table 1: *Gasification process*

Process	**Biomass**	**Reactor**	**Catalytic**	**Products**
Gasification	Glycerol with lignocellulosic	Fixed Bed		Syngas
Gasification	Sawdust	Fluidized Bed	Fe/CaO	Syngas
Gasification	Lignocellulosic materials	Tubular		Hydrogen
Gasification	Wood	-		Syngas
Gasification	Glycerol	Fluidized Bed		Syngas
Gasification	Refuse fuels	Tubular		Syngas
Gasification and Pyrolysis	Pine sawdust	Tubular	Nickel	Syngas
Gasification and Pyrolysis	Rubber	Tubular		Hydrogen and Syngas
Gasification and Pyrolysis	Food waste	Tubular		Syngas
Gasification and Pyrolysis	Pine sawdust	Fluidized Bed	Dalomite and Nickel	Syngas

Biomass gasification is a renewable alternative that has the potential to decrease CO_2 emissions. However, efficient energy and resource utilization is essential. Previous works had shown that biomass is most cost-effectively used for heating purposes or electricity generation. But to increase the overall efficiency, biomass gasification could be integrated in industrial processes. The gasification is an old thermo-chemical conversion technology with a change of the chemical structure of the biomass at 800 - 1000 ºC in the presence of a gasifying agent (for instance air, oxygen, steam, CO_2, or mixtures of these components) enables the promotion of steam and dry reforming reactions and thus it consists another method of producing a H_2 rich gas from biomass.

Air has been broadly used as the oxygen source for gasification. There are numerous researches that dis cussed the performance of biomass gasification process with/without air and steam (table 1). Though, this technology with steam requires additional energy cost for increasing the temperature of supplementary steam. Due to the economic perspective, it was gained attention and consideration on the low temperature biomass gasification with air and steam. Since the steam gasification reaction is an endothermic reaction, air is also used to decrease the energy cost by partial oxidation (exothermic reaction) reaction of biomass (Chang et al., 2011) that also known as dry methane reforming.

2.4 The Reaction of the Dry Methane Reforming

For more than 80 years, the steam methane reforming (SMR) has been the preferred method for the industrial production of hydrogen either as a pure gas or as a reactant for the production of ammonia or methanol (Adilson et. al 2008). More recently, syngas reforming technologies and downstream conversion processes have attracted attention as promising options for the conversion of carbon containing sources into clean fuels via Fischer-Tropsch processes (Mohamad Hassan Amin et. al. 2010). Methane(CH_4) can be converted with Carbon Dioxide (CO_2) to yield or produce the mixture of gaseous of hydrogen (H_2) and Carbon Monoxide (CO) that known as Syngas or Synthesis gaseous according to the respective equations.

Carbon Dioxide reduction by Methane:

$$\boldsymbol{CO_2 + CH_4 \leftrightarrow 2CO + 2H_2} \qquad \Delta H_{298}^{0} = +247\frac{kJ}{mol} \cdots\cdots\cdots\cdots (1)$$

The main reaction of Dry Methane reforming (DMR) is described in equation 1, and this reaction is endothermic which requires heat. In thermodynamics, the term endothermic describes a process or reaction in which the system absorbs energy from its surroundings in the form of heat. From equation 1, which is

Methane (CH_4) reacts with Carbon Dioxide (CO_2) on the active surface of solid catalyst to form equimolar synthesis gas. Excess Carbon Dioxide (CO_2) is required to increase the conversion of the reaction. As been explained before, the gas Carbon Dioxide (CO_2) is harmful to the environment as well as human being. Then for this reaction to take place, a right amount of Methane(CH_4) need to be applied to this reaction to reduce Carbon Dioxide (CO_2) and convert it into synthesis gas or syngas. This reaction typically takes place over Ni-based catalysts at the temperature from 550℃ - 1000℃ (Tungkamani et al. 2013).

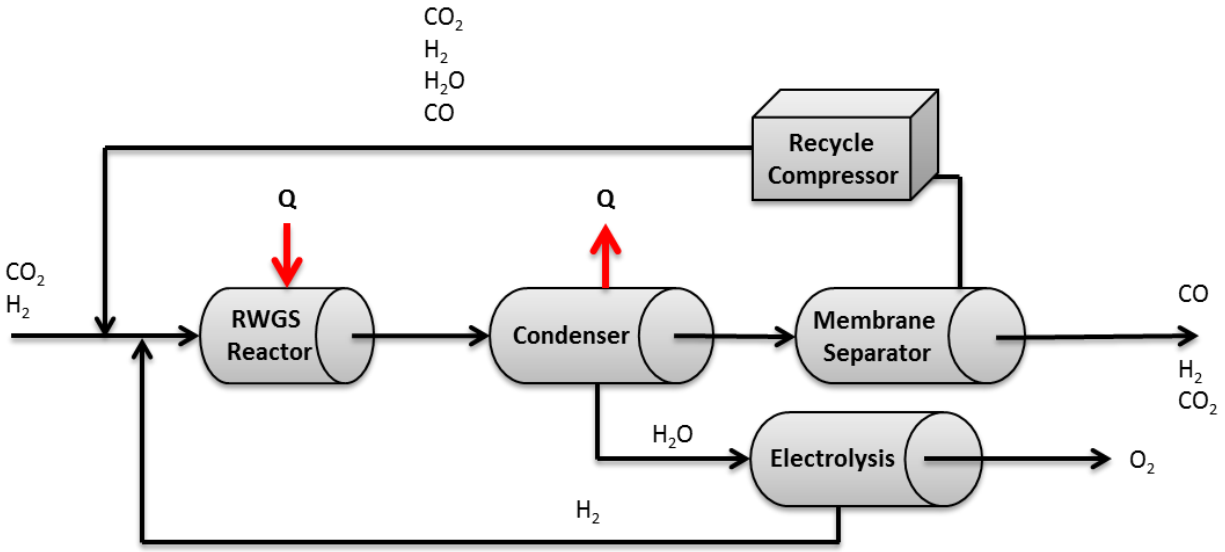


Figure 3: *Reverse water-gas shift flow cycle*

Reverse water-gas shift (RWGS) reaction:

$$\boldsymbol{CO_2 + H_2 \leftrightarrow CO + H_2O} \cdots\cdots\cdots\cdots (2)$$

The reverse water-gas shift reaction (RWGS) describes the reaction of Carbon Dioxide (CO_2) and hydrogen (H_2) to form of Carbon Monoxide (CO) and water vapor (H_2O). Because the reverse water-gas shift reaction (equation 2) is also accompanied with Dry Methane reforming (DMR) reaction, the excess Carbon Dioxide (CO_2) and generated hydrogen (H_2) can be converted into Carbon Monoxide (CO). The reversibility of the WGSR is important in the production of ammonium, methanol, and Fischer–Tropsch synthesis where the ratio of H_2/CO is critical. Typically, it is done

using a copper on aluminium catalyst (Al-ali et al. 2013). Many other industrial companies exploit the reverse water gas shift reaction (RWGS) reaction as a source of the synthetically valuable CO from cheap CO_2 (Lim et al. 2012).

Methane decomposition:

$$\boldsymbol{CH_4 \leftrightarrow C + 2H_2} \qquad \Delta \quad 5 \quad -75.3\ \frac{kJ}{mol} \cdots\cdots\cdots\cdots (3)$$

Reverse Boudouard reaction:

$$\boldsymbol{C + CO_2 \leftrightarrow 2CO} \qquad \Delta H^0_{298} = -172\ \frac{kJ}{mol} \cdots\cdots\cdots\cdots (4)$$

Accordingly, the amount of hydrogen (H_2) generated by Dry Methane reforming (DMR) is less than that produced in the steam reforming process. Dry Methane reforming (DMR) seems more appropriate for the use of biogas mixtures since no CO_2 separation steps are required and both C atoms (one from CH_4 and another from CO_2) are incorporated into the final product, decreasing waste production. It has been reported that there are various types of carbon formation on No-based catalyst during Dry Methane reforming (DMR) (Masashi Hishada et al. 2011). Throughout this formation there are respectively carbon deposition on catalyst results primarily from the following reactions which are equation 3 and 4. At high temperature, the Boudouard reaction is thermodynamically limited and it desirable to operate at high temperature. However, methane decomposition is favored at high temperature to minimize the thermodynamic driving force for carbon deposition from these two reactions. Catalysts that can inhibit carbon formation kinetically at conditions where carbon formation is thermodynamically favorable are desirable.

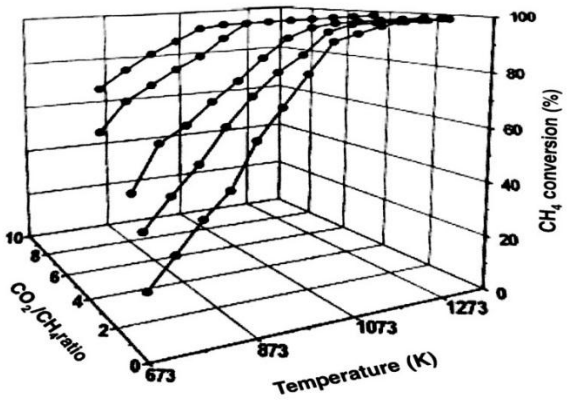


Figure 4: *Calculated thermodynamics conversion of methane for various CO2/CH4 ratios as function of temperature.*

2.5 Modeling of Dry Methane Reforming Kinetics Reaction Model

In chemical reaction engineering, simulations are very useful and valuable for investigating and optimizing a particular reaction process or system. For this project, which is "The development of reaction kinetics model for the production of Synthesis gas from Carbon Dioxide (CO_2): Dry Methane Reforming" the MATLAB simulation software will be used to investigate the process parameter through Dry Methane reforming (DMR) reaction as well as calculation of reaction rate constant (k)by using MATLAB optimization tollbox.

There are few studies or research regarding the development of kinetics reaction model of Dry Methane Reforming (DRM). For example, Unni Ilsbye et al. (1997) reported that Kinetic studies of Dry Methane Reforming over a highly active Ni/La/R-Al_2O_3 catalyst were performed in an atmospheric micro-catalytic fixed bed reactor. On this studied, the reaction temperature was varied between 700°C and 900 °C, while partial pressures of Carbon Dioxide CO_2 and Methane CH_4 ranged from 16kPa to 40 kPa. The result of his research, the measurement of kinetic parameters which is the activation energy was determined. Apart from that, Unni Ilsbye et al. (1997) explained that the rate of CO_2 reforming was described by applying a Langmuir- Hinshelwood rate equation and the developed kinetics was interpreted with a two-phase model of a fluidized bed.

Later, different approach from Maher et al. (2003) which is on their research they investigated that cobalt-tungsten *è*-carbide material (CO_6W_6C) as an originator for a stable and active catalyst for the dry reforming of methane to produce synthesis gas. The kinetics of CH_4/CO_2 reforming were studied under differential conditions over a temperature range of 500°C - 600 °C, based on a his detailed experimental design. Maher et al. (2003) observed that rates qualitatively follow a Langmuir-Hinshelwood type of reaction mechanism. Such a scheme is considered quantitatively, with four reactions which are methane reforming, reverse water-gas shift, carbon deposition, and carbon removal by a reverse Boudouard reaction. Of these, carbon deposition and carbon removal are generally disregarded in most of the reported kinetic models.

Say Yei Foo et. al. then investigated regarding the CO_2 reforming of CH_4 in the presence of O_2 in the feed of fixed bed reactor containing a Co-Ni catalyst. From his research, its show that important of temperature, pressure on each reaction that affects the reaction rate constant(k). In additional from his results, the H_2: CO product ratio increased from 0.9 for pure CO_2 reforming and peaked at 1.73 as O2 partial pressure increased to an equimolar level in the feed. The increased reaction temperature resulted in lower H_2: CO due to increased CO_2 reforming kinetics. The post reaction analysis revealed that even mild O_2 dosing leads to negligible carbon deposition. Thus, this form of reactor operation is energetically attractive and provided efficient carbon utilization.

In 2014, Khalid Al-Ali et. al. had developed Modeling and simulation of the reforming behavior of a mixture of methane and carbon dioxide in a direct-contact bubble reactor (DCBR). Throughout his research, the endothermic catalytic reaction obeys the kinetics of the methane dry reforming in a direct-contact bubble reaction system that containing an active catalyst which are Ni–Al2O3 catalyst and molten salt mixture system. The reforming process was simulated, using commercial software for chemical kinetics, for a single reactor model, to examine a kinetic model based on the postulated heterogeneous reaction mechanism, in the temperature range 600–900 degree C, at 1 atm. The simulated data were evaluated and validated with the measured data

from a laboratory reformer. The catalyst activity in the DCBR was characterized using a catalyst–bubble contact model, in terms of the total-catalytic active surface area. Khalid Al-Ali et. al. used the detailed simulation studies to identify the essential characteristics of the reaction mechanism in a DCBR.

For this project which is, "The Development Reaction Kinetics Model for production of Hydrocarbon is from Carbon dioxide" is studied based on the parametric study of the reaction kinetics model with general used of catalyst. At the last, the validation of the results will be compared with previous study.

2.6 Arrhenius Equation: Temperature control and measurement

In this project, all the independent variables such as activation energy and reaction rate constant are evaluated through the simulation. The rate law is an expression relating the rate of a reaction to the concentrations of the chemical species present, which may include reactants, products, and catalysts. Many reactions follow a simple rate law.

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$

*E*a is the activation energy for the reaction, and *A* is a constant known as the pre exponential factor. This temperature dependence means that in order to measure an accurate value for *k*, the temperature of the reaction mixture must be maintained at a constant, known value. If activation energies are to be measured as part of the kinetic study, rate constants must be measured at a series of temperatures.

CHAPTER 3: METHODOLOGY

Methodology is the systematic, theoretical analysis of the methods applied to a field of study. It comprises the theoretical analysis of the body of methods and principles associated with a branch of knowledge. Typically, it encompasses concepts such as paradigm, theoretical model, phases and quantitative or qualitative techniques.

3.1 Research Methodology

The methodology used in performing the research can be divided into five (5) parts:

I. Selection of a process

One process has to be studied in which the process is chosen from the reference paper. Characteristics and parameters of Methane reforming process model had been chosen for further study based on the topics itself. Preliminary study on past researched based on related topic and issue that related to this topic. Variables of the project is identified through various reading and consideration.

By utilizing the gases produced from landfills which are mainly Carbon Dioxide (CO_2) and Methane(CH_4), the parameters from the process is studied based on many variables. Dry Methane Reforming (DMR) tends to minimize the cost, but the same time maximize and utilize the two major greenhouse gases which are, Carbon Dioxide (CO_2) and Methane(CH_4) to form more valuable product which is Hydrogen that meet the market demands.

II. Process Modelling

Process modelling will represents the whole process. Based on 4 main equations which are Carbon Dioxide (CO_2) reduction by Methane(CH_4), Reverse Water-

Gas Shift (RWGS) equation, Methane Decomposition and Reverse Boudouard equation are simulated in MATLAB simulation. Familiarize with the process simulation software

III. Analysis of design and tuning parameters

The analysis on the design of DMR kinetics model and tuning parameters of DMR had to be done. The analysis will be done in terms of simulation by using MATLAB software. The analysis of the tuning parameters will lead to the best tuning parameters condition to achieve high performance or high efficiency of production of valuable product which is Hydrogen. The best parameters can be achieved and as a basic parameters for future references for this type of reaction. The simulation will run for the DMR production process and process parameter is study by varies the value. Throughout this study, Reaction Rate Constant (k) will be calculated by using MATLAB optimization toolbox.

IV. Validity of the information

The results from graph will be analyze and compare to current information from various research paper for validity. Throughout this project the behavior of each variable of parameter will be studied (Parametric study)

3.2 Gantt Chart

The project will be carried out methodically based on the following timeline:

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■								
2	Submission of Progress Report							●								
3	Project Work Continues								■	■	■	■	■			
4	Pre-SEDEX										●					
5	Submission of Draft Final Report											●				
6	Submission of Dissertation (soft bound)												●			
7	Submission of Technical Paper												●			
8	Viva													●		
9	Submission of Project Dissertation (Hard Bound)															●

● Suggested milestone

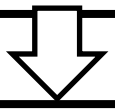
■ Process

3.3 Project Flowchart & Key Milestone

PROBLEM STATEMENT & OBJECTIVE OF THE PROJECT

Identify the purpose of this research project.

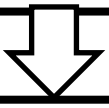
- **OBJECTIVES:** To develop the reaction kinetics model for the Dry Reforming of Methane. To perform parametric study for the hydrocarbon production from Carbon Dioxide (CO_2) and Methane(CH_4) utilization and to calculate the reaction kinetics constant using optimization approach (MATLAB simulation).
- **PROBLEM STATEMENT:** Due to the frequent production of landfill gas, the increase in pressure within the landfill causes the gases release into the atmosphere that mainly affect the climate change and global warming.



LITERATURE REVIEW

Gather information from journals, research papers and etc.

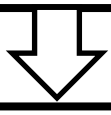
- To study the fundamental knowledge and concepts of utilization of Methane and Carbon Dioxide gases to form value added product such as Hydrogen from Dry Methane Reforming. Study of their applications and past research from various type of research papers.



MATLAB ACTIVITIES

Define all variables and starting write a

- All the variables are identified through literature review.
- Development Reaction Kinetics Model by using MATLAB. Run the simulation for the DMR production process and varies the process parameter.



EXPERIMENT DESIGN

Identify the subjects that need to be investigated and experimental procedures as well as the collection of data

- Construct and run the simulation for the DMR production process and varies the process parameter. Calculation of Reaction Rate Constant (k)by using MATLAB

DATA ANALYSIS AND INTERPRETATION

Findings obtained are analyzed and interpreted critically.

- Results will be analyzed using MATLAB and Microsoft Excel. The aim is to determine the optimum parameters configuration for Dry Methane Reforming process.
- Parametric study of the reaction kinetics model of Dry Methane Reforming (DRM).

DOCUMENTATION AND REPORTING

The whole research project will be documented and reported in detail. Recommendations or aspects that can be further improved in the future will be discussed.

3.3.1 MATLAB Activities

Simulation study of Dry Methane Reforming (DMR) has a good way in terms of design parametic study as it provides good inter-related parameters process for basic and future references. The existence of problems commonly in the waste disposal center (Landfills) can be overcome by optimize the used of two major greenhouse gases which are, Carbon Dioxide (CO_2) and Methane(CH_4) production from solid waste. The application of Dry Methane Reforming (DMR) processes is widely used in industry. Besides, the modeling of DMR is necessary for references. Therefore, DMR model is a convenient way to illustrate the modeling principles through simulated using MATLAB Simulation Software.

In solving the problem related to this simulation, script M-files or function M-files is required in MATLAB Simulation Software. This method actually creates a function, with inputs and outputs. Throughout this M-file, all initial guess independent variables such as the reaction kinetics constant (K) and activation energy (AE) are defined for optimization. Optimization is the selection of a best element from some set of available alternatives. In the simplest case, an optimization problem consists of maximizing or minimizing a real function by systematically choosing input values from within an allowed set and computing the value of the function. The example of algorithm files of MATLAB function files are shown in APPENDIX.

3.3.2 Developed of Function M-files

Most of the M-files that one eventually uses will be function M-files. These files again have the ".m" extension, but they are used in a different way than scripts. Function files have input and output arguments. Examples function M-files that have been created are for Dry Methane Reforming are:

I. Calc_Constant_Rate.m

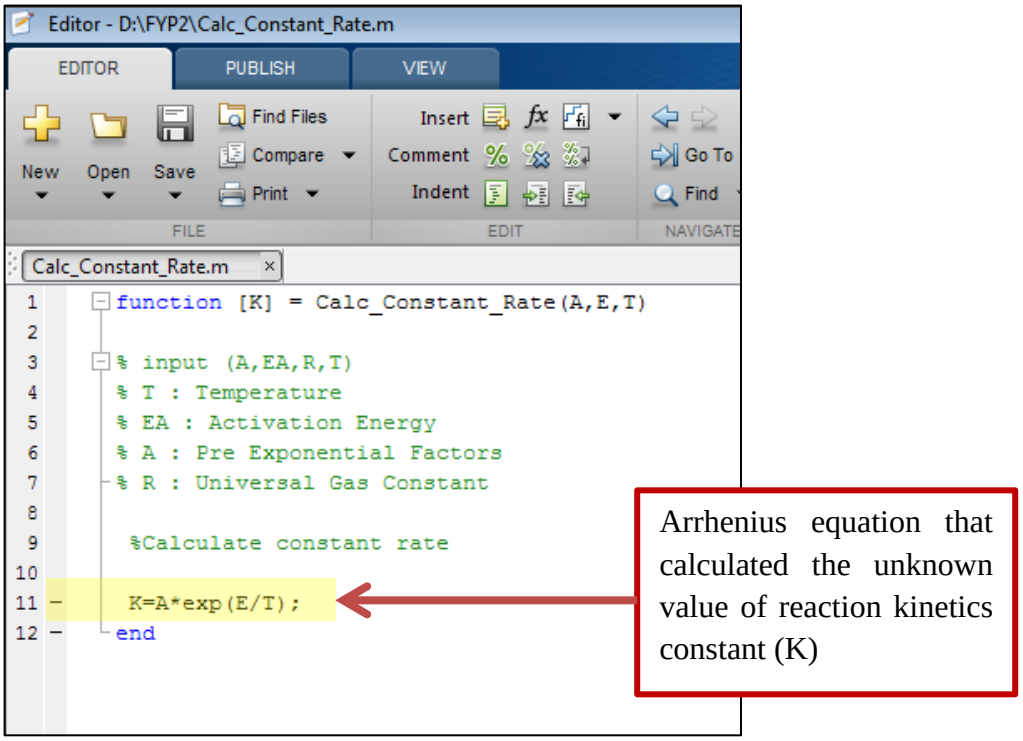


Figure 5: *Creating the Arrhenius equation within function M-files*

II. Run_Constant_Rate.m

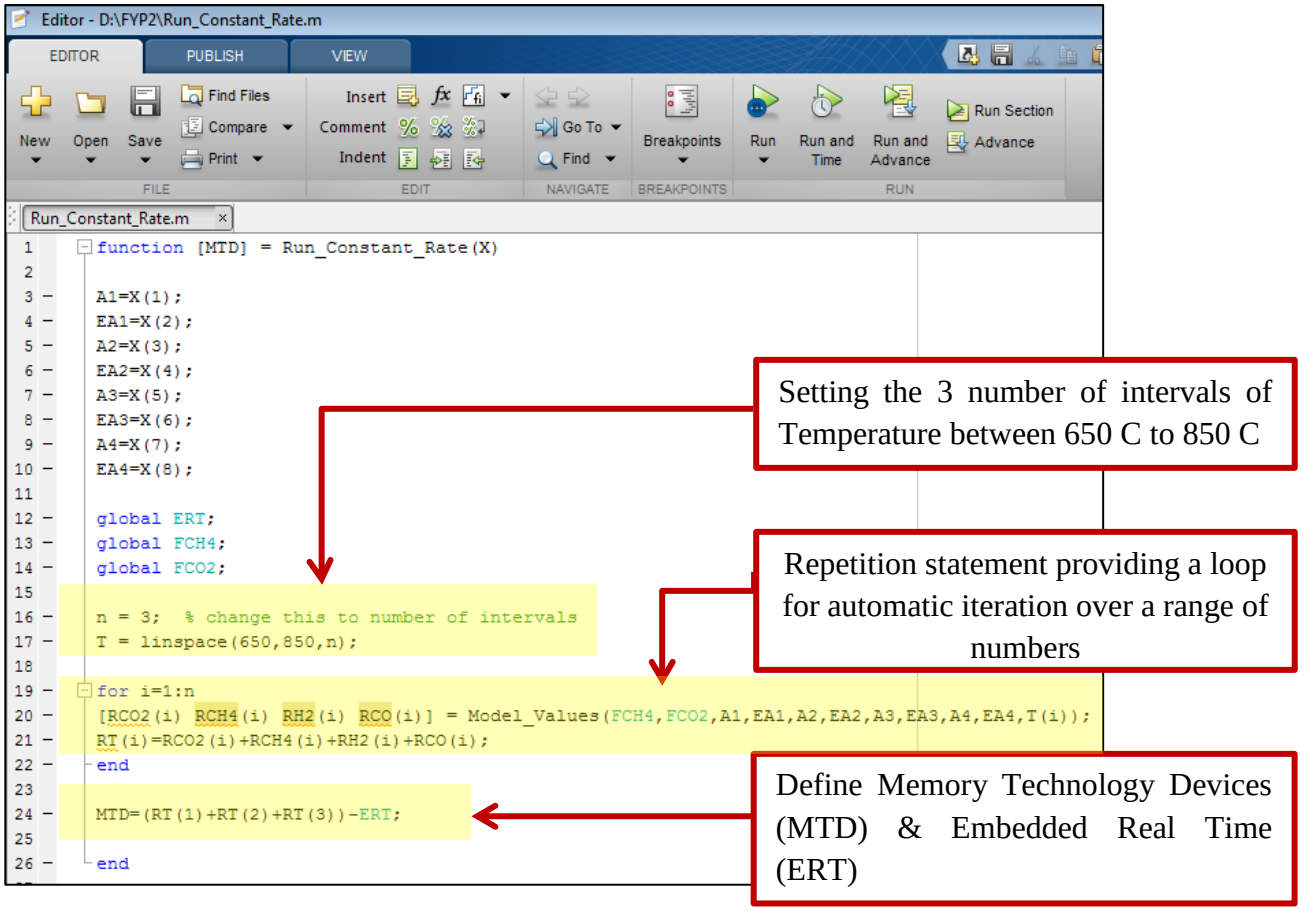


Figure 6: *Specify the operating condition using MATLAB*

III. Model_Values.m

Run_Constant_Rate.m | Model_Values.m

```
1   function[RCO2 RCH4 RH2 RCO] = Model_Values(FCH4,FCO2,A1,EA1,A2,EA2,A3,EA3,A4,EA4,T)
2
3   %Calculate Constant rate through Arrhenius Equation
4   [K1]=Calc_Constant_Rate(A1,EA1,T);
5   [K2]=Calc_Constant_Rate(A2,EA2,T);
6   [K3]=Calc_Constant_Rate(A3,EA3,T);
7   [K4]=Calc_Constant_Rate(A4,EA4,T);
8
9   r1 = K1*FCO2*FCH4;
10  r2 = K2*FCO2*r1;
11  r3 = K3*FCH4;
12  r4 = K4*r3*FCO2;
13
14  %Carbon Dioxide
15      rCO2 = -r1-r2-r4;
16  %Methane
17      rCH4 = -r3-r1;
18  %Carbon
19      rC = r3-r4;
20  %Hydrogen
21      rH2 = r1-r2+2*r3;
22  %Carbon Monooxide
23      rCO = 2*r1+r2+2*r4;
24  %Water
25      rH2O = r2;
26
27      %compositions (mol%) of product gas
28
29  RT=rCO2+rCH4+rH2+rCO;
30
31  RCO2=rCO2*100/RT;
32  RCH4=rCH4*100/RT;
    RCO=rCO*100/RT;
    RH2=rH2*100/RT;

    end
```

Calculation of Reaction kinetics constant (K) of each reaction based on previous defined function M-files (Calc_Constant_Rate)

Calculation of composition of product gas

Figure 7: *Function file for calculation of product composition.*

IV. Constant_Rate_Contraints

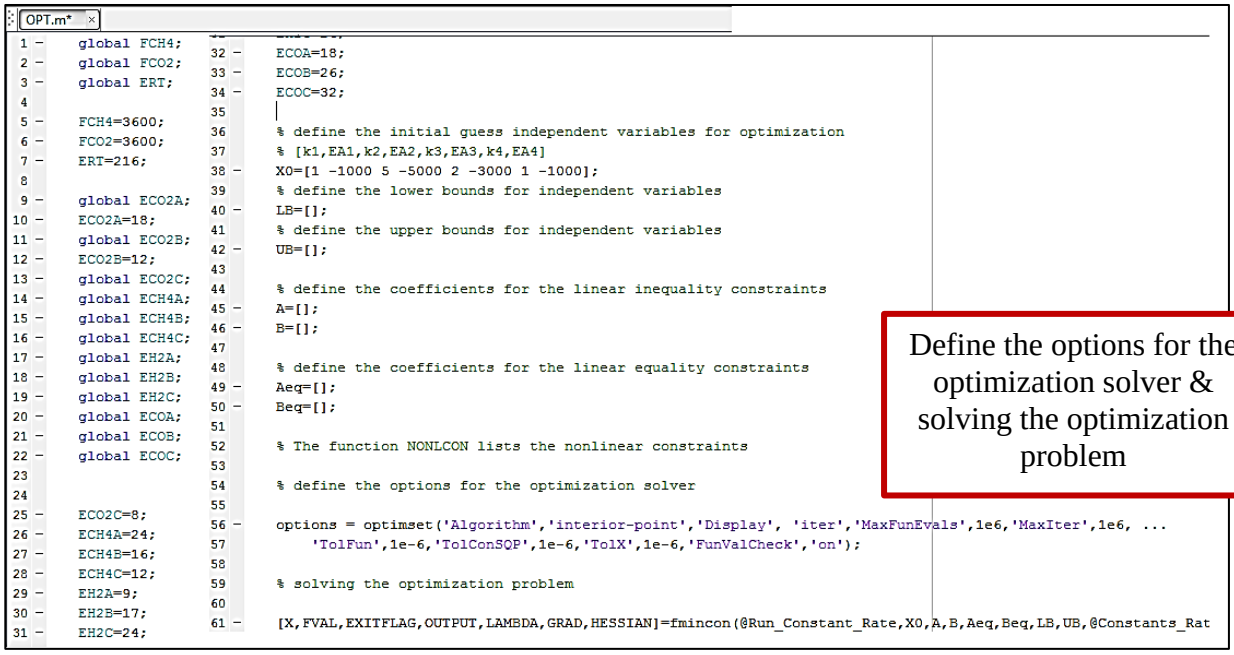
Constants_Rate_Constraints.m*

```
function[c,ceq] = Constants_Rate_Constraints(X)
A1=X(1);
EA1=X(2);
A2=X(3);
EA2=X(4);
A3=X(5);
EA3=X(6);
A4=X(7);
EA4=X(8);
global FCH4;
global FCO2;

n=3;  % change this to number of intervals
T = linspace(650,850,n);

for i=1:n
[RCO2(i) RCH4(i) RH2(i) RCO(i)] = Model_Values(FCH4,FCO2,A1,EA1,A2,EA2,A3,EA3,A4,EA4,T(i));

end
ceq=[];
global ECO2A;
global ECO2B;
global ECO2C;
global ECH4A;
global ECH4B;
global ECH4C;
global EH2A;
global EH2B;
global EH2C;
global ECOA;
global ECOB;
global ECOC;


c(1)=ECO2A-RCO2(1);
c(2)=ECO2B-RCO2(2);
c(3)=ECO2C-RCO2(3);

c(4)=ECH4A-RCH4(1);
c(5)=ECH4B-RCH4(2);
c(6)=ECH4C-RCH4(3);

c(7)=EH2A-RH2(1);
c(8)=EH2B-RH2(2);
c(9)=EH2C-RH2(3);

c(10)=ECOA-RCO(1);
c(11)=ECOB-RCO(2);
c(12)=ECOC-RCO(3);


end
```

Define the all the variables as global.

Figure 8: *Function file of constant rate constraints*

V. OPT.m

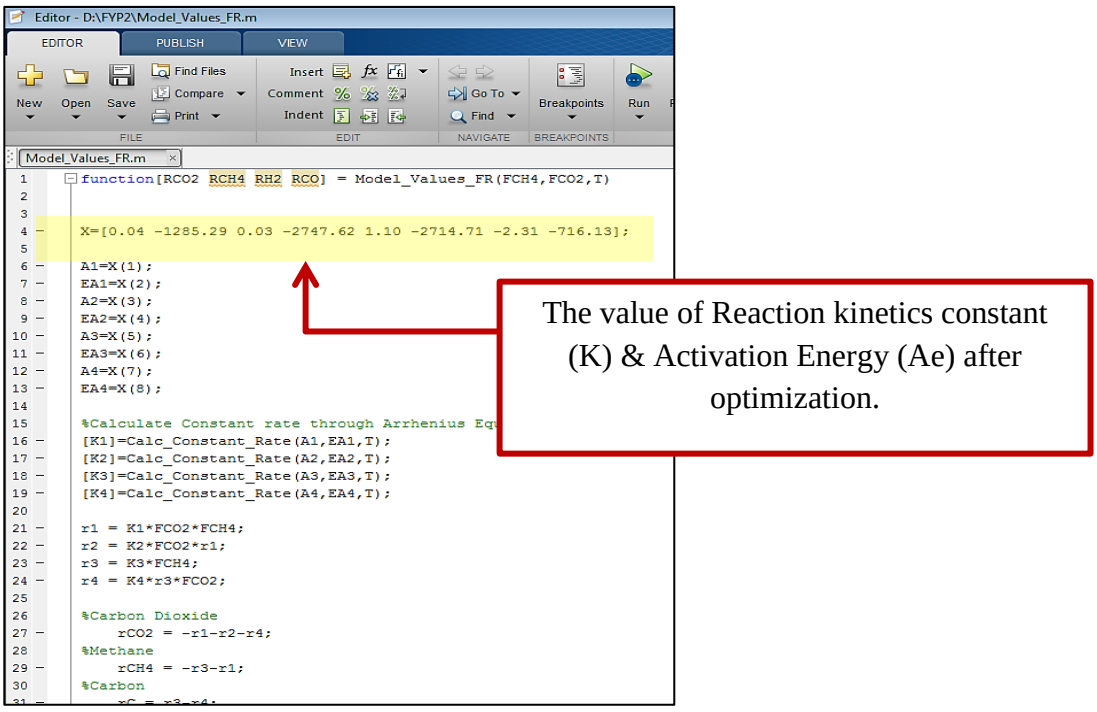


```
OPT.m*
1  - global FCH4;
2  - global FCO2;
3  - global ERT;
4
5  - FCH4=3600;
6  - FCO2=3600;
7  - ERT=216;
8
9  - global ECO2A;
10 - ECO2A=18;
11 - global ECO2B;
12 - ECO2B=12;
13 - global ECO2C;
14 - global ECH4A;
15 - global ECH4B;
16 - global ECH4C;
17 - global EH2A;
18 - global EH2B;
19 - global EH2C;
20 - global ECOA;
21 - global ECOB;
22 - global ECOC;
23
24
25 - ECO2C=8;
26 - ECH4A=24;
27 - ECH4B=16;
28 - ECH4C=12;
29 - EH2A=9;
30 - EH2B=17;
31 - EH2C=24;
32 - ECOA=18;
33 - ECOB=26;
34 - ECOC=32;
35
36   % define the initial guess independent variables for optimization
37   % [k1,EA1,k2,EA2,k3,EA3,k4,EA4]
38 - X0=[1 -1000 5 -5000 2 -3000 1 -1000];
39   % define the lower bounds for independent variables
40 - LB=[];
41   % define the upper bounds for independent variables
42 - UB=[];
43
44   % define the coefficients for the linear inequality constraints
45 - A=[];
46 - B=[];
47
48   % define the coefficients for the linear equality constraints
49 - Aeq=[];
50 - Beq=[];
51
52   % The function NONLCON lists the nonlinear constraints
53
54   % define the options for the optimization solver
55
56 - options = optimset('Algorithm','interior-point','Display', 'iter','MaxFunEvals',1e6,'MaxIter',1e6, ...
57       'TolFun',1e-6,'TolConSQP',1e-6,'TolX',1e-6,'FunValCheck','on');
58
59   % solving the optimization problem
60
61 - [X,FVAL,EXITFLAG,OUTPUT,LAMBDA,GRAD,HESSIAN]=fmincon(@Run_Constant_Rate,X0,A,B,Aeq,Beq,LB,UB,@Constants_Rat
```

Define the options for the optimization solver & solving the optimization problem

Figure 9: *Function file of optimization.*

VI. Model_Values_FR.m



```
Editor - D:\FYP2\Model_Values_FR.m
EDITOR | PUBLISH | VIEW
New | Open | Save | Find Files | Compare | Print | Insert | Comment | Indent | Go To | Find | Breakpoints | Run
FILE | EDIT | NAVIGATE | BREAKPOINTS
Model_Values_FR.m
1  - function[RCO2 RCH4 RH2 RCO] = Model_Values_FR(FCH4,FCO2,T)
2
3
4  -   X=[0.04 -1285.29 0.03 -2747.62 1.10 -2714.71 -2.31 -716.13];
5
6  -   A1=X(1);
7  -   EA1=X(2);
8  -   A2=X(3);
9  -   EA2=X(4);
10 -   A3=X(5);
11 -   EA3=X(6);
12 -   A4=X(7);
13 -   EA4=X(8);
14
15     %Calculate Constant rate through Arrhenius Eq
16 -   [K1]=Calc_Constant_Rate(A1,EA1,T);
17 -   [K2]=Calc_Constant_Rate(A2,EA2,T);
18 -   [K3]=Calc_Constant_Rate(A3,EA3,T);
19 -   [K4]=Calc_Constant_Rate(A4,EA4,T);
20
21 -   r1 = K1*FCO2*FCH4;
22 -   r2 = K2*FCO2*r1;
23 -   r3 = K3*FCH4;
24 -   r4 = K4*r3*FCO2;
25
26     %Carbon Dioxide
27 -       rCO2 = -r1-r2-r4;
28     %Methane
29 -       rCH4 = -r3-r1;
30     %Carbon
```

The value of Reaction kinetics constant (K) & Activation Energy (Ae) after optimization.

Figure 10: *Function file of model values.*

3.3.3 Data Analysis and Interpretation

After optimization process, a parametric study will be conducted. Parametric study is the analysis or examination between different parameters. The objective of this parametric study is to examine common behavior pattern of configurations in term of graph to determine the influence parameters to feeds consumption and product production. For this parametric study of the reaction kinetics model of Dry Methane Reforming (DMR) process, the process will be illustrated and simulated using MATLAB Simulation Software for the further study on variation of the process parameter study. The operational parametric that will be study are Methane to Carbon Dioxide (CH_4/CO_2) ratio on feed stream, reaction temperature of the Dry Methane Reforming (DRM) process as well as syngas synthesis. Parametric study for Dry Methane Reforming (DRM) process synthesis will be refer as previous study of Dry Methane Reforming (DRM) process from various study and journal. Throughout these journals, there are many facts and knowledge can be used for this study. The research procedures for this study are, understand the background for chemical reaction of the Dry Methane Reforming (DRM) process. Then develop the chemical reaction equation of the whole process and identification of the variables (operating parameters) for the process.

CHAPTER 4: RESULTS AND FINDINGS

4.1 Gas phase reactions: Effects of using same inlet Molar Composition Ratio

Inlet Gas Flow = $\mathbf{3600}\frac{\boldsymbol{ml}}{\boldsymbol{hr}}$

Molar Composition (inlet) $CH_4 : CO_2 = \mathbf{1}:\mathbf{1}$

Reaction Temperature Range = $\mathbf{650}℃ - \mathbf{850}℃$

Table 2: *Initial and final Guess of Independent Variables for optimization*

No	Initial Guess		Final Guess	
	Reaction rate constant(k)	**Activation Energy (E_a)**	**Reaction rate constant(k)**	**Activation Energy (E_a)**
1	1	-1000	0.04	-1285.29
2	5	-5000	0.03	-2747.62
3	2	-3000	1.10	-2714.71
4	1	-1000	-2.31	-716.13

Table 3: *Table of relationship between Mole Percentage (%) and Temperature (℃)*

Component	650℃	670℃	690℃	710℃	730℃	750℃	770℃	790℃	810℃	830℃	850℃
CO2	8.06	6.07	4.65	3.65	2.95	2.48	2.18	2.01	1.95	1.97	2.05
CH4	34.31	29.69	26.01	23.03	20.57	18.52	16.79	15.32	14.05	12.95	11.99
H2	19.69	23.32	26.30	28.78	30.88	32.70	34.28	35.67	36.91	38.02	39.02
CO	37.91	40.90	43.02	44.53	45.58	46.28	46.73	46.98	47.07	47.00	46.92

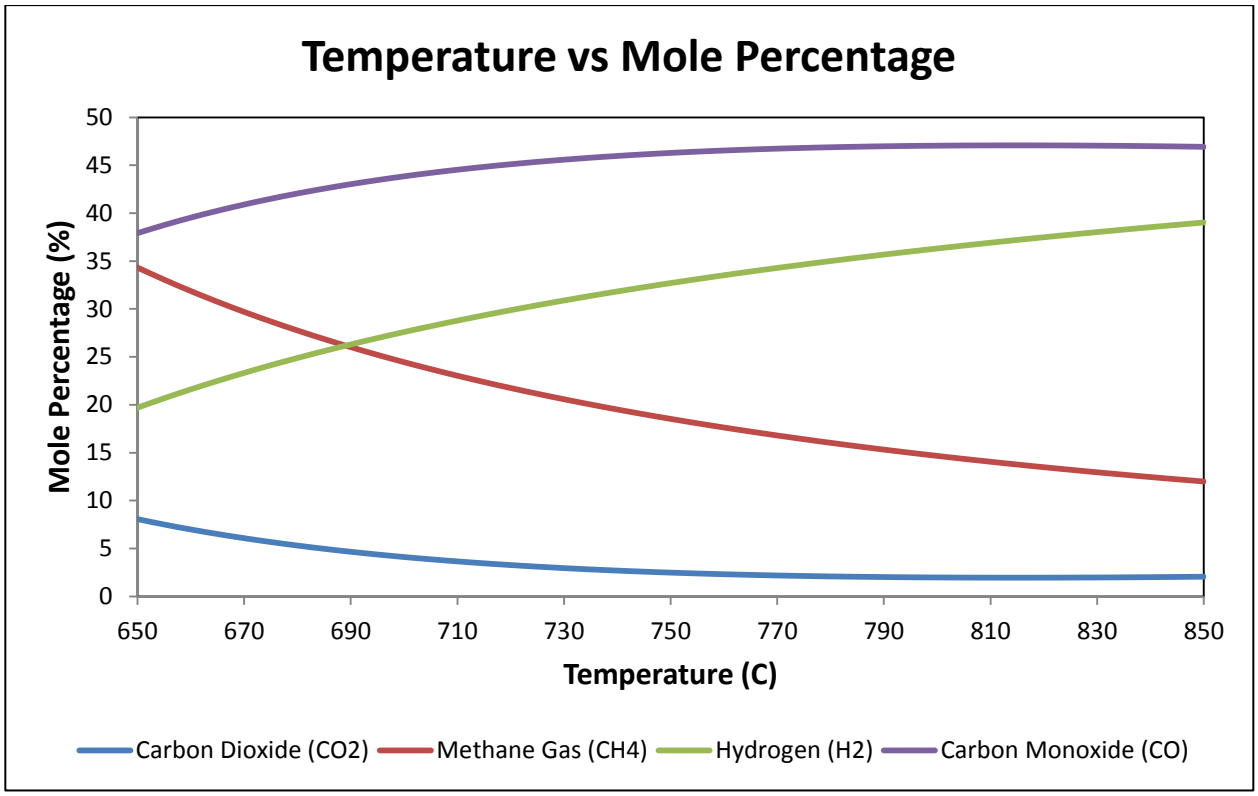


Figure 11: *Graph of outlet Mole Percentage (%) at different Temperature (℃)*

Experiment data obtained through optimization in MATLAB Simulation Software. Constant inlet gas feed flow was set at $3600\frac{ml}{hr}$ with $CH_4{:}\,CO_2 = 1{:}\,1$. There are no catalyst involve since this is general simulation for Dry Methane Reforming. Figure 11 shows a predicted results using kinetics model with the experimental data, in terms of CH_4 and CO_2conversions. This model was able to predict the Methane (CH_4) reforming experimental data reasonably well, especially for Methane (CH_4), Carbon Dioxide (CO_2), Carbon Monoxide (CO) and Hydrogen (H_2) in terms of graph patterns and changes of mole percentages with increasing temperature. However, the model underestimates the experimental all components conversions, this is attributed to variations of initial Guess of independent variables as a results of the final value of independent variables after optimization. Figure 11 shows the influence of reaction temperature from 650℃ to 900℃ on the methane dry reforming reaction. As the

reaction temperature increased, the Methane (CH_4) and Carbon Dioxide (CO_2), conversions both significantly increased.

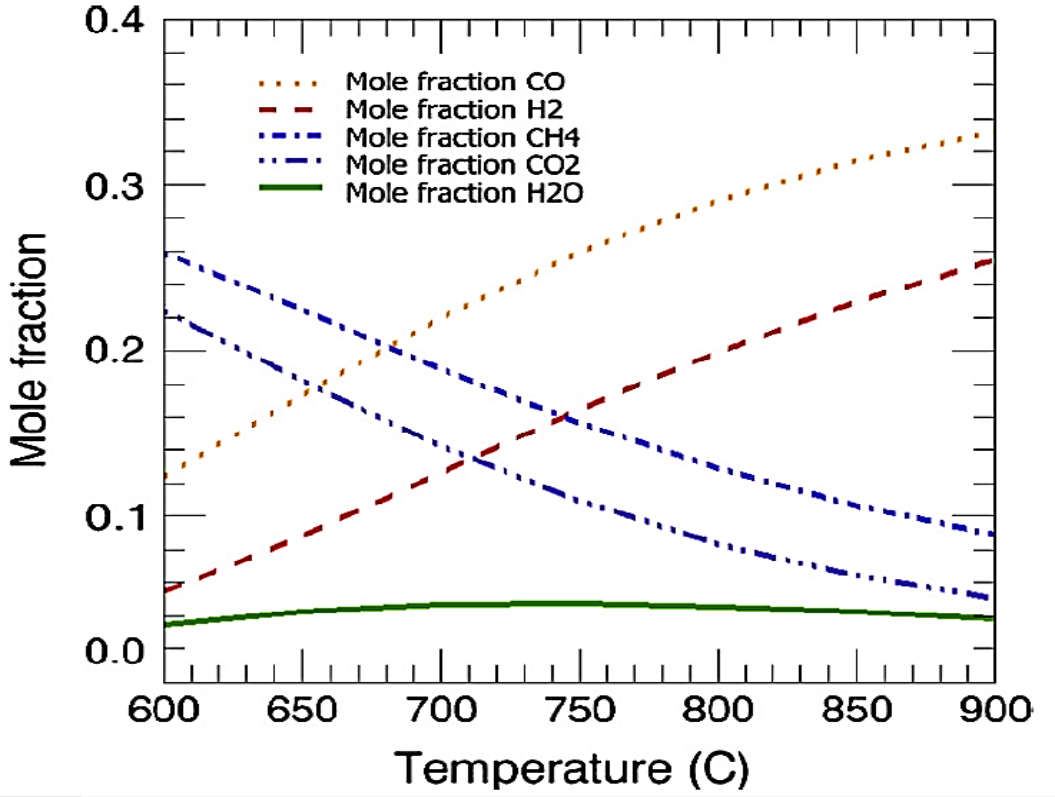


Figure 12: *Graph of outlet Mole Percentage (%) at different Temperature (℃)*

(Khalid Al Ali et al 2013)

It can be seen in a same pattern between in figure 11 and 12, the pattern of graph of predicted through optimization in MATLAB simulation software is shown at figure 10 meanwhile figure 12 shows the references of reaction that have been conducted by K.Al-Ali et all (2014). Figure 11 shows the influence of reaction temperature from $\mathbf{650}℃ - \mathbf{750}℃$ on the methane dry reforming reaction. As the reaction temperature increased, the Methane (CH_4) and Carbon Dioxide (CO_2) conversions both significantly increased. As a result of the undesirable formation of water during the reaction, different reaction rates for Methane (CH_4) and Carbon Dioxide (CO_2) were observed. The Carbon Dioxide (CO_2) conversions were always greater than the Methane (CH_4) that are clearly shown in figure 11. The H_2/CO production ratio was less tha unity as shown in figure 11.

4.3 Gas phase reactions: Effects of using different Molar Composition Ratio (Inlet)

Inlet Gas Flow = $\mathbf{3600}\frac{\boldsymbol{ml}}{\boldsymbol{hr}}$

Molar Inlet Ratio $CH_4 : CO_2 = \mathbf{3}:\mathbf{1}$

Reaction Temperature Range = $\mathbf{650}℃ - \mathbf{850}℃$

Table 4: *Initial and final Guess of Independent Variables for optimization*

No	Initial Guess		Final Guess	
	Reaction rate constant(k)	**Activation Energy (E_a)**	**Reaction rate constant(k)**	**Activation Energy (E_a)**
1	1	-1000	0.04	-1285.29
2	5	-5000	0.03	-2747.62
3	2	-3000	1.10	-2714.71
4	1	-1000	-2.31	-716.13

Table 5: *Table of relationship between Mole Percentage (%) and Temperature (℃) with different Molar Inlet Ratio*

Ratio		650℃	670℃	690℃	710℃	730℃	750℃	770℃	790℃	810℃	830℃	850℃
CH_4	CO_2											
1	**1**	8.06	6.07	4.65	3.65	2.95	2.48	2.18	2.01	1.95	1.97	2.05
		34.31	29.69	26.01	23.03	20.57	18.52	16.79	15.32	14.05	12.95	11.99
3	**1**	8.06	6.07	4.65	3.65	2.95	2.48	2.18	2.01	1.95	1.97	2.05
		34.31	29.69	26.01	23.03	20.57	18.52	16.79	15.32	14.05	12.95	11.99
1	**3**	8.06	6.07	4.65	3.65	2.95	2.48	2.18	2.01	1.95	1.97	2.05
		34.31	29.69	26.01	23.03	20.57	18.52	16.79	15.32	14.05	12.95	11.99

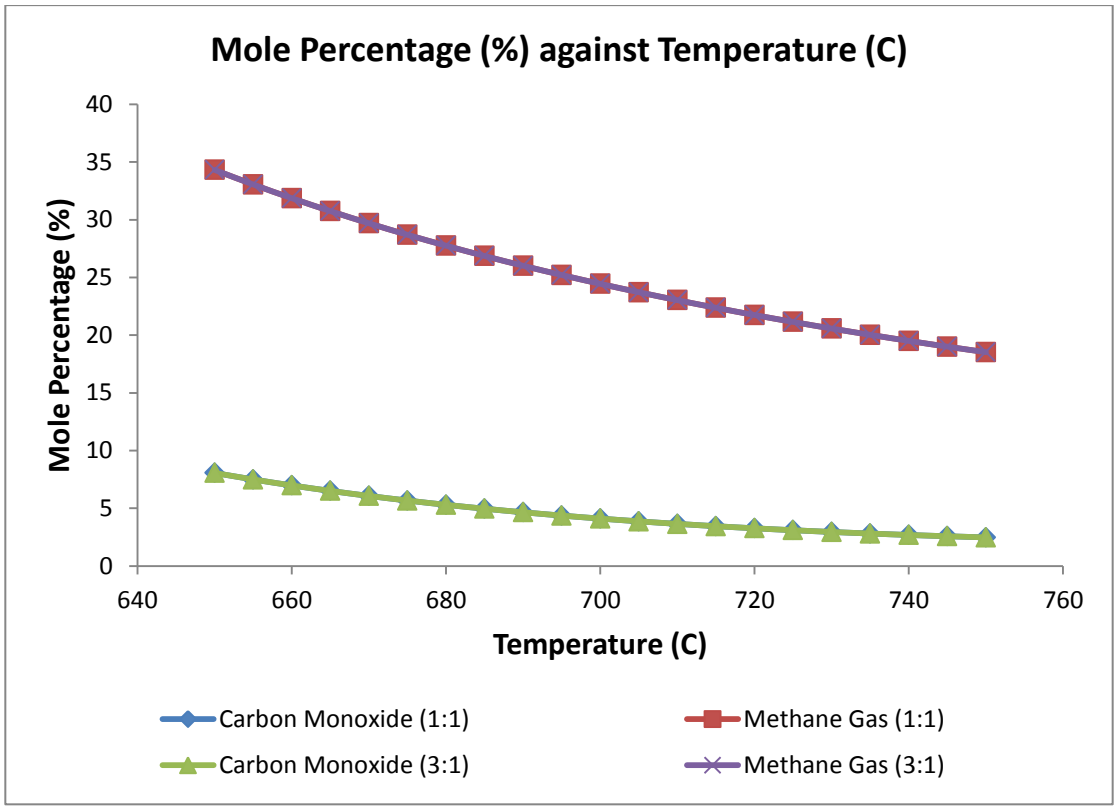


Figure 13: *Graph of outlet Mole Percentage (%) at different Temperature (℃) with different Molar Inlet Ratio*

Figure 13 shows a comparison of the predicted results with molar inlet ratio ($CH_4: CO_2 = 3:1$) with predicted results with molar inlet ratio ($CH_4: CO_2 = 1:1$). Although, in the rich of Methane (CH_4) mixture reforming reaction which is ratio ($CH_4: CO_2 = 3:1$), the carbonates (CH_4) compensate or balance the shortcoming of Carbon Dioxide (CO_2) indicating the same predicted results as previous which is with molar inlet ratio ($CH_4: CO_2 = 1:1$). There is no change of feed mole of percentage consumption as shows in figure 13.

4.3 Gas phase reactions: Effects of using same Molar Composition Ratio (Inlet) with increasing inlet gas flow

4.3.1 Inlet Gas Flow = $\mathbf{3600}\frac{\boldsymbol{ml}}{\boldsymbol{hr}}$

Molar Composition (inlet) $CH_4 : CO_2 = \mathbf{1}:\mathbf{1}$

Reaction Temperature Range = $\mathbf{650}℃ - \mathbf{850}℃$

Table 6: *Initial and final guess value of Independent Variables of optimization*

No	Initial Guess		Final Guess	
	Reaction rate constant(k)	**Activation Energy (E_a)**	**Reaction rate constant(k)**	**Activation Energy (E_a)**
1	1	-1000	0.04	-1285.29
2	5	-5000	0.03	-2747.62
3	2	-3000	1.10	-2714.71
4	1	-1000	-2.31	-716.13

Table 7: *Table of relationship between Mole Percentage (%) and Temperature (℃) with different Molar Inlet Ratio (CH4:CO2=1:1) at Inlet Gas Flow = 3600 ml/hr*

Component	650℃	670℃	690℃	710℃	730℃	750℃	770℃	790℃	810℃	830℃	850℃
CO2	8.06	6.07	4.65	3.65	2.95	2.48	2.18	2.01	1.95	1.97	2.05
CH4	34.31	29.69	26.01	23.03	20.57	18.52	16.79	15.32	14.05	12.95	11.99
H2	19.69	23.32	26.30	28.78	30.88	32.70	34.28	35.67	36.91	38.02	39.02
CO	37.91	40.90	43.02	44.53	45.58	46.28	46.73	46.98	47.07	47.00	46.92

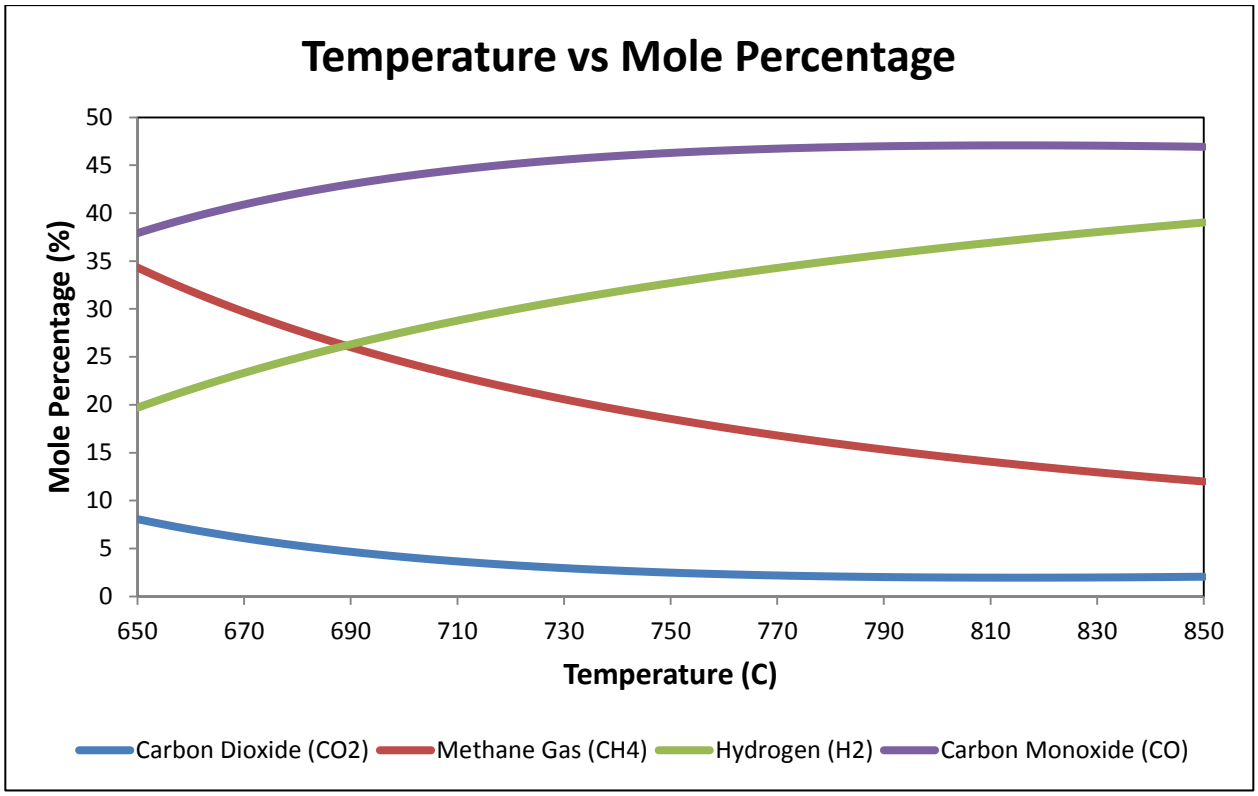


Figure 14: *Graph of Mole Percentage (%) at different Temperature (℃) with different Molar Inlet Ratio (CH4:CO2=1:1) at Inlet Gas Flow = 3600 ml/hr*

Figure 14, 15 and 16 shows that the influence of inlet gas flow (ml/hr) on the Dry Methane Reforming reaction. As the inlet gas flow increased, Methane (CH_4) and Carbon Dioxide (CO_2) conversions both gradually decreased. As a result the formation of product which is syngas in decreased. The negative value of Carbon Monoxide (CO) in figure 14 shows that the inlet gas flow which is $7200\,\frac{ml}{hr}$ is not suitable with the range of reaction temperature $650℃ - 850℃$. The higher the gas flow the higher the temperature needed for the reactions.

4.3.2 Inlet Gas Flow = $\mathbf{5400}\frac{\boldsymbol{ml}}{\boldsymbol{hr}}$

Molar Inlet Ratio$CH_4 : CO_2 = \mathbf{1}:\mathbf{1}$

Reaction Temperature Range = $\mathbf{650}℃ - \mathbf{850}℃$

Table 8: *Initial and final guess value of Independent Variables of optimization*

No	Initial Guess		Final Guess	
	Reaction rate constant(k)	**Activation Energy (E_a)**	**Reaction rate constant(k)**	**Activation Energy (E_a)**
1	1	-1000	0.04	-1285.29
2	5	-5000	0.03	-2747.62
3	2	-3000	1.10	-2714.71
4	1	-1000	-2.31	-716.13

Table 9: *Relationship between Mole Percentage (%) and Temperature (℃) in different Molar Inlet Ratio (CH4:CO2=1:1) with Inlet Gas Flow = 5400 ml/hr*

Component	650℃	670℃	690℃	710℃	730℃	750℃	770℃	790℃	810℃	830℃	850℃
CO_2	27.62	25.76	24.43	23.48	22.82	22.37	22.08	21.93	21.87	21.89	21.96
CH_4	27.00	23.46	20.61	18.28	16.35	14.74	13.37	12.20	11.19	10.31	9.54
H2	36.79	39.41	41.59	43.45	45.04	46.43	47.66	48.75	49.73	50.62	51.42
CO	8.57	11.36	13.35	14.78	15.77	16.44	16.87	17.10	17.19	17.16	17.05

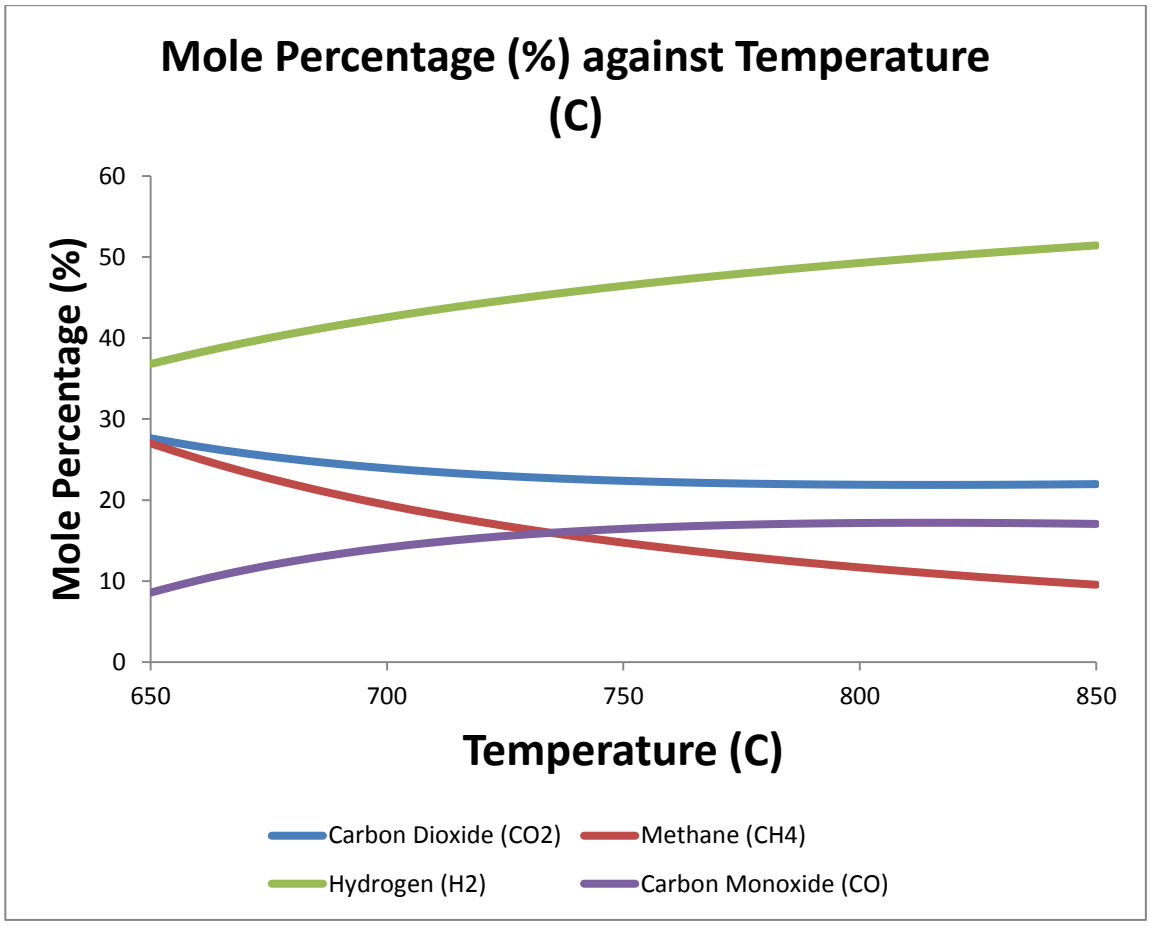


Figure 15: *Graph of Mole Percentage (%) at different Temperature (℃) with different Molar Inlet Ratio (CH4:CO2=1:1) at Inlet Gas Flow = 5400 ml/hr*

4.3.3Inlet Gas Flow = $\mathbf{7200}\frac{\boldsymbol{ml}}{\boldsymbol{hr}}$

Molar Inlet Ratio$CH_4 : CO_2 = \mathbf{1}:\mathbf{1}$

Reaction Temperature Range = $\mathbf{650}℃ - \mathbf{850}℃$

Table 10: *Initial and final Guess value of Independent Variables of optimization*

No	Initial Guess		Final Guess	
	Reaction rate constant(k)	**Activation Energy (E_a)**	**Reaction rate constant(k)**	**Activation Energy (E_a)**
1	1	-1000	0.04	-1285.29
2	5	-5000	0.03	-2747.62
3	2	-3000	1.10	-2714.71
4	1	-1000	-2.31	-716.13

Table 11: *Relationship between Mole Percentage (%) and Temperature (℃) in different Molar Inlet Ratio (CH4:CO2=1:1) with Inlet Gas Flow = 7200 ml/hr*

Component	650℃	670℃	690℃	710℃	730℃	750℃	770℃	790℃	810℃	830℃	850℃
CO_2	40.31	38.62	37.41	36.54	35.93	35.52	35.26	35.11	35.06	35.07	35.15
CH_4	22.26	19.39	17.06	15.11	13.57	12.24	11.10	10.13	9.30	8.57	7.93
H2	47.88	49.91	51.63	53.10	54.38	55.51	56.51	57.41	58.22	58.96	59.63
CO	-10.46	-7.93	-6.11	-4.81	-3.89	-3.28	-2.89	-2.67	-2.59	-2.61	-2.72

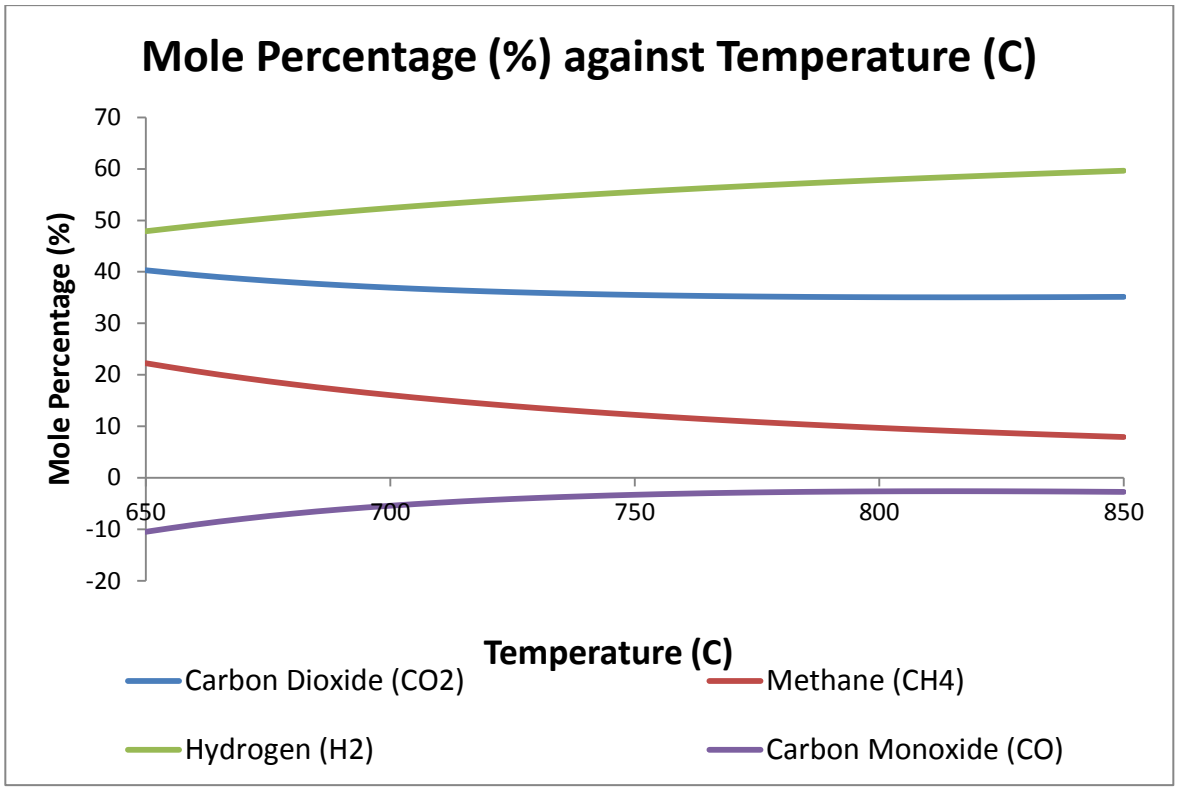


Figure 16: *Graph of Mole Percentage (%) at different Temperature (℃) with different Molar Inlet Ratio (CH4:CO2=1:1) at Inlet Gas Flow = 7200 ml/hr*

Figure 14 shows the results obtained from predicted results after optimization, the inlet gas flow was increased by 2 times from $3600\frac{ml}{hr}$ to $7200\frac{ml}{hr}$. The graph shows when the influence of inlet gas flow is significantly important as the inlet gas flow increased, the Methane (CH_4) and Carbon Dioxide (CO_2) conversions both bit by bit increased. The negative value of Carbon Monoxide (CO) shows that the inlet gas flow which is $7200\frac{ml}{hr}$ is not suitable with the range of temperature $650℃ - 850℃$. The higher the gas flow the higher the temperature needed for the reactions. Whereas, for the inlet gas velocity of $5400\frac{ml}{hr}$, the syngas production is not produced in maximum value. For this reason, an optimization strategy was applied to understand the trade-off between high production rate and high CO_2 and CH_4 consumption rate in Dry Methane Reforming. For more effective optimization approach to maximize use of the entire reactant (inlet gas), a suitable inlet gas flow need to identified to produce highest productions of Synthesis gas.

CHAPTER 5: CONCLUSIONS

This research study expected to fulfill the main objective which is successfully to develop the reaction kinetics model for the Dry Methane Reforming and to perform parametric study for the hydrogen production from Greenhouse gases that produced from landfills gas which are Carbon Dioxide (CO_2) and Methane(CH_4) as well as to calculate the reaction kinetics constant using optimization approach (MATLAB simulation). An effective tool, the Dry Methane Reforming model, was developed to evaluate all the independent variables of activation energy value and reaction kinetics constant value (k). This value signifies how effectively all the independent variables towards the reaction of producing syngas that can be refer as general kinetics model for Dry Methane Reforming as a future references.

Based on detailed simulation studies, the important characteristics of the reaction mechanism of Dry Methane Reforming were identified. Gas phase kinetics has a significant consequence towards the production of syngas. The higher the temperature, the better the conversion achieved until a certain limit. In agreement with the experimental observations, the reaction temperature is considered to be one of the most influential independent variables. Based on the effects of using same molar composition ratio (Inlet) with increasing inlet gas flow results, the designer can conclude that the inlet gas flow in a gas phase reactions is also dominant to the reactions. It has significant effect to the reactions whereas inlet molar composition ratio of the reactions has no significant effect.

CHAPTER 6: REFERENCES

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APPENDIXES

1. Calculate Constant Rate MATLAB file

```
function [K] = Calc_Constant_Rate(A,E,T)

% input (A,EA,R,T)
% T : Temperature
% EA : Activation Energy
% A : Pre Exponential Factors
% R : Universal Gas Constant

 %Calculate constant rate

 K=A*exp(E/T);
end
```

2. Run Constant Rate MATLAB File

```
function [MTD] = Run_Constant_Rate(X)

A1=X(1);
EA1=X(2);
A2=X(3);
EA2=X(4);
A3=X(5);
EA3=X(6);
A4=X(7);
EA4=X(8);

global ERT;
global FCH4;
global FCO2;

n = 3;  % change this to number of intervals
T = linspace(650,850,n);

for i=1:n
[RCO2(i) RCH4(i) RH2(i) RCO(i)] =
Model_Values(FCH4,FCO2,A1,EA1,A2,EA2,A3,EA3,A4,EA4,T(i));
RT(i)=RCO2(i)+RCH4(i)+RH2(i)+RCO(i);
end

MTD=(RT(1)+RT(2)+RT(3))-ERT;

end
```

3. OPT MATLAB File

```
global FCH4;
global FCO2;
global ERT;

FCH4=3500;
FCO2=3500;
ERT=216;

global ECO2A;
ECO2A=18;
global ECO2B;
ECO2B=12;
global ECO2C;
global ECH4A;
global ECH4B;
global ECH4C;
global EH2A;
global EH2B;
global EH2C;
global ECOA;
global ECOB;
global ECOC;


ECO2C=8;
ECH4A=24;
ECH4B=16;
ECH4C=12;
EH2A=9;
EH2B=17;
EH2C=24;
ECOA=18;
ECOB=26;
ECOC=32;



% define the initial guess independent variables for optimization
% [k1,EA1,k2,EA2,k3,EA3,k4,EA4]
X0=[1 -1000 5 -5000 2 -3000 1 -1000];
% define the lower bounds for independent variables
LB=[];
% define the upper bounds for independent variables
UB=[];

% define the coefficients for the linear inequality constraints
A=[];
B=[];

% define the coefficients for the linear equality constraints
Aeq=[];
```

```
Beq=[];

% The function NONLCON lists the nonlinear constraints

% define the options for the optimization solver

options = optimset('Algorithm','interior-point','Display',
'iter','MaxFunEvals',1e6,'MaxIter',1e6, ...
    'TolFun',1e-6,'TolConSQP',1e-6,'TolX',1e-6,'FunValCheck','on');

% solving the optimization problem

[X,FVAL,EXITFLAG,OUTPUT,LAMBDA,GRAD,HESSIAN]=fmincon(@Run_Constant_Rate
,X0,A,B,Aeq,Beq,LB,UB,@Constants_Rate_Constraints,options);
```

4. Model Values FR

```
function[RCO2 RCH4 RH2 RCO] = Model_Values_FR(FCH4,FCO2,T)


X=[0.04 -1285.29 0.03 -2747.62 1.10 -2714.71 -2.31 -716.13];

A1=X(1);
EA1=X(2);
A2=X(3);
EA2=X(4);
A3=X(5);
EA3=X(6);
A4=X(7);
EA4=X(8);

%Calculate Constant rate through Arrhenius Equation
[K1]=Calc_Constant_Rate(A1,EA1,T);
[K2]=Calc_Constant_Rate(A2,EA2,T);
[K3]=Calc_Constant_Rate(A3,EA3,T);
[K4]=Calc_Constant_Rate(A4,EA4,T);

r1 = K1*FCO2*FCH4;
r2 = K2*FCO2*r1;
r3 = K3*FCH4;
r4 = K4*r3*FCO2;

%Carbon Dioxide
    rCO2 = -r1-r2-r4;
%Methane
    rCH4 = -r3-r1;
%Carbon
    rC = r3-r4;
%Hydrogen
    rH2 = r1-r2+2*r3;
%Carbon Monooxide
    rCO = 2*r1+r2+2*r4;
%Water
    rH2O = r2;


%compositions of product gas

RT=rCO2+rCH4+rH2+rCO;

RCO2=rCO2*100/RT;
RCH4=rCH4*100/RT;
RCO=rCO*100/RT;
RH2=rH2*100/RT;


end
```

5. Constants Rate Constraints

```
function[c,ceq] = Constants_Rate_Constraints(X)

A1=X(1);
EA1=X(2);
A2=X(3);
EA2=X(4);
A3=X(5);
EA3=X(6);
A4=X(7);
EA4=X(8);

global FCH4;
global FCO2;

n=3;  % change this to number of intervals
T = linspace(650,850,n);

for i=1:n
[RCO2(i) RCH4(i) RH2(i) RCO(i)] =
Model_Values(FCH4,FCO2,A1,EA1,A2,EA2,A3,EA3,A4,EA4,T(i));

end
ceq=[];


global ECO2A;
global ECO2B;
global ECO2C;
global ECH4A;
global ECH4B;
global ECH4C;
global EH2A;
global EH2B;
global EH2C;
global ECOA;
global ECOB;
global ECOC;


c(1)=ECO2A-RCO2(1);
c(2)=ECO2B-RCO2(2);
c(3)=ECO2C-RCO2(3);

c(4)=ECH4A-RCH4(1);
c(5)=ECH4B-RCH4(2);
c(6)=ECH4C-RCH4(3);

c(7)=EH2A-RH2(1);
c(8)=EH2B-RH2(2);
c(9)=EH2C-RH2(3);

c(10)=ECOA-RCO(1);
```

```
c(11)=ECOB-RCO(2);
c(12)=ECOC-RCO(3);


end
```

6. Constants Rate Constraints

```
function[RCO2 RCH4 RH2 RCO] =
Model_Values(FCH4,FCO2,A1,EA1,A2,EA2,A3,EA3,A4,EA4,T)

%Calculate Constant rate through Arrhenius Equation
[K1]=Calc_Constant_Rate(A1,EA1,T);
[K2]=Calc_Constant_Rate(A2,EA2,T);
[K3]=Calc_Constant_Rate(A3,EA3,T);
[K4]=Calc_Constant_Rate(A4,EA4,T);

r1 = K1*FCO2*FCH4;
r2 = K2*FCO2*r1;
r3 = K3*FCH4;
r4 = K4*r3*FCO2;

%Carbon Dioxide
    rCO2 = -r1-r2-r4;
%Methane
    rCH4 = -r3-r1;
%Carbon
    rC = r3-r4;
%Hydrogen
    rH2 = r1-r2+2*r3;
%Carbon Monooxide
    rCO = 2*r1+r2+2*r4;
%Water
    rH2O = r2;

    %compositions (mol%) of product gas

RT=rCO2+rCH4+rH2+rCO;

RCO2=rCO2*100/RT;
RCH4=rCH4*100/RT;
RCO=rCO*100/RT;
RH2=rH2*100/RT;

end
```